

STUDIES ON CARBOXYMETHYLCELLULOSE

Part VI.—Preparation and Properties of Potassium Carboxymethylcellulose

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It was confirmed that K-carboxymethylcellulose cannot be prepared directly from K-cellulose and monochloroacetic acid in aqueous medium. But it could be successfully prepared in aqueous-ethanolic medium according to new method developed in this laboratory.

Process variables and the effect on D.S. were studied. The reaction was found to depend on factors more or less similar to that found for Na-carboxymethylcellulose except that the best D.S. (1.19) was obtained in absolute alcohol medium. The D.S. could be increased with repetitive carboxymethylation and in four stages a value of 2.11 was obtained (compared to 2.63 reported earlier⁹ for Na-carboxymethylcellulose).

Results are presented on physical properties, detergency improving properties and emulsifying ability. K-carboxymethylcellulose was considered better than Na-carboxymethylcellulose for the preparation of cod-liver oil-water emulsion.

Introduction

Na-carboxymethylcellulose has, particularly during the last 20 years, developed itself into an important commercial product having an increasing number of uses. Details will be found in a recent review.¹ In all the above cases only the use of sodium Na-carboxymethylcellulose has been mentioned and the methods of commercial preparation²⁻⁴ have not differed fundamentally from the original laboratory reaction of combining sodium monochloroacetate to the alkali cellulose in an aqueous medium. In most of the commercial products available, the degree of substitution varies from 0.6 to 0.8 when the products are just water soluble but serve the purpose in detergent industry which was its main use.

In this laboratory, the main interest on carboxymethylation was to explore the possibility of utilization of jute, first after delignification and then directly as such in place of cotton linters or paper pulp. Another purpose was to modify the conditions and the process as to get the products having higher degrees of substitution which might have other interesting properties. Emulsification of oil-water suspension was found to be one such property.

Initially it was found that by using very high concentration of alkali, the degree of substitution could be increased in aqueous medium to 1.05 and in this respect both cotton and delignified jute were more or less equally good.⁵ Later, an excellent method⁶ was developed in this laboratory by using water-organic solvents as reaction medium. The process was simplified by combining the

carboxymethylation with the prior preparation of soda cellulose. For results obtained in ethanolic medium, water-cellulose ratio was a critical factor. With an overall alkali concentration of 17% (w/v) and with a water-cellulose ratio of 1.0 from purified jute, a degree of substitution of 1.31 was obtained. Interestingly enough it was later observed that better carboxymethylation was obtained⁷ if the process was carried out directly with crude jute powder (without delignification). And in a single step a D.S. of 1.48 was obtained. The same reaction could be further pushed forward by carrying in an autoclave⁸ and a D.S. of 1.61 was achieved. Repetitive carboxymethylation was last attempted⁹ in which by four step repetitive treatment a D.S. of above 2.6 was obtained with jute whereas with cotton after the fifth step a value of 2.88 was achieved; the properties of this product were a bit different.

All the above work concerned with Na-carboxymethylcellulose. Very little information was available for the corresponding potassium salt. Hollabough, Burt and Walsh¹⁰ described the resemblance in some properties of the two compounds, but did not mention the method of preparation of K-salt. Hader, Waldeck and Smith⁴ believe that metal carboxymethylcellulose can be prepared from Na-carboxymethylcellulose with metal salts in aqueous solution by double decomposition. Longworth and J. J. Hermans¹¹ prepared K-carboxymethylcellulose from Na-carboxymethylcellulose by treatment with KCl.

In the present work also it was first found that in an aqueous medium, potassium carboxymethylcellulose could not be prepared; but in ethanolic

(or aqueous-ethanolic) medium, with potassium hydroxide and monochloroacetic acid, the reaction proceeds as smoothly as sodium carboxymethylcellulose. The following report describes the different process variables that affect the overall reaction.

Experimental

Purification of Cotton

Cotton was procured from local market, powdered and refluxed with 2:1 benzene-ethanol solvent in the usual way for dewaxing. The dewaxed cotton was treated with 1% alkali till the alkali-treated solution was colourless. It was then thoroughly washed with distilled water, dried and stored in a vacuum desiccator.

(a) *Carboxymethylation in Aqueous Medium.*—Five g purified cotton was taken for each experiment and steeped in aqueous KOH (having desired concentration) at 28–30°C for 2 hr. To this an 80% aqueous solution of monochloroacetic acid was added dropwise from a burette while the mass was kept stirred. The carboxymethylation was then continued for 6 hr at 30–45°C. The product was insoluble in water.

(b) *Carboxymethylation in Aqueous-ethanolic Medium.*—To prepare K-carboxymethylcellulose in aqueous-ethanolic medium, 5 g purified cotton was steeped in KOH in water-ethanol (1:6 by volume) at 28–30°C for 2 hr. To this an 80% ethanolic solution of monochloroacetic acid was added dropwise and carboxymethylation was continued for 6 hr at 30–45°C.

The crude K-carboxymethylcellulose was treated with water to make a 2% solution. Sometimes, the product was partially soluble in water. Otherwise, the product was completely soluble in water.

When the product was partially soluble in water, the slurry was carefully filtered through cloth filter. The cake obtained was treated again with sufficient water to recover any residual amount of K-carboxymethylcellulose and then refiltered. The clear solution together with the wash liquor was treated with 80–90% ethanol to precipitate out pure K-carboxymethylcellulose. When the product was completely soluble in water, no filtration was necessary. K-carboxymethylcellulose could be precipitated out directly by adding 80–90% ethanol. The precipitate was allowed to settle, and the upper portion of the solution was decanted. After filtration over cloth filter, K-carboxymethylcellulose was dried. The filtrate and decanted liquor were distilled to re-

cover ethanol. The degree of substitution was determined by uranyl gravimetric method.¹²

(c) *Repetitive Carboxymethylation.*—It was observed⁹ during the preparation of highly substituted Na-carboxymethylcellulose by repetitive carboxymethylation that better results can be obtained if the (main bulk of the) undried product is used for further carboxymethylation.

In the present investigation, to get a highly substituted K-carboxymethylcellulose, by repetitive carboxymethylation, we therefore used undried product. A certain portion of dry K-carboxymethylcellulose, prepared in the early stage, was dissolved in a minimum volume of water and precipitated by 80–90% ethanol. The precipitate was washed three times with absolute alcohol. The washed liquor was squeezed out as much as possible and the wet product was treated with a calculated amount of KOH solution and subsequently carboxymethylated, following the same procedure as described earlier.

(d) *Surface Tension.*—Surface tension of solutions of K-carboxymethylcellulose in water and solutions containing mixtures of a laundry soap and K-carboxymethylcellulose having different D.S. values were measured with the help of a Jung-type torsion balance applying the bow method

Results and Discussion

While studying the different aspects of preparation of K-carboxymethylcellulose, it was considered proper to reattempt to prepare the potassium salt directly in aqueous medium. Experiments were carried out under similar conditions to those for preparation of Na-carboxymethylcellulose in aqueous medium, but using potassium hydroxide of concentrations varying between 17.5–70.0%. But under all circumstances the product obtained was insoluble in water from which it was concluded that the average degree of substitution (if any reaction has taken place) is extremely low. Although no convincing and definite reason for this sluggishness of this reaction with caustic potash can at once be given, it may be relevant to indicate that K-carboxymethylcellulose had only been prepared from Na-carboxymethylcellulose according to the report available.¹¹

Our aim being the preparation of highly substituted K-carboxymethylcellulose, a direct method was more convenient. And since earlier in our laboratory^{6,7} for preparation of Na-carboxymethylcellulose, an aqueous-ethanolic medium was found to produce much better result than simple aqueous medium, the natural approach was to

try the process out for K-carboxymethylcellulose, and surprisingly the process responded quite satisfactorily. The first series of experiments were carried out with all working conditions, solvent composition and water-cellulose ratio; the same as was found optimum earlier, but the KOH concentration was varied from 17.5% to 40.0% (Table 1). With 17.5% KOH, K-carboxymethylcellulose having a very low D.S. of 0.18 was obtained. The product also contained large amount of unreacted fibres. As the concentration of KOH was increased to 24.5%, a marked increase in degree of substitution (0.68) was observed and the product was completely soluble in water. With further increase of the caustic potash concentration, the substitution increased fairly steadily up to 30% and then slowed down beyond 35%. It should be noted that the degree of substitution obtained with even 35% caustic potash (1.04) was less than that obtained under similar condition for Na-carboxymethylcellulose (D.S.=1.23) with 17.5% NaOH. Calculating on the

molecular basis, results with 17.5% caustic soda are comparable with 24.5% caustic potash. Considering this, it should be taken that although quite uniform water-soluble K-carboxymethylcellulose (D.S.=1.04) can be successfully prepared directly from cotton in aqueous-ethanolic KOH medium, the reaction appears somewhat sluggish compared to that for sodium preparation.

An explanation for this can be had from the work of Heuser and Bartunek,¹³ who had studied the absorption of alkali and the swelling of cellulose in different concentrations of various alkali hydroxide solution. They observed that swelling and absorption increase with alkali concentration. In case of KOH, maximum swelling of cellulose (and also the limit in the absorption curve) was at 32% KOH, whereas that for NaOH was at 18%. This also supports our earlier postulation that overall carboxymethylation process was somehow connected with the absorption of alkali.

Effect of Water/Cellulose Ratio

It had been observed that water alone was not sufficient to activate cellulose for ensuring carboxymethylation by KOH. But by ethanol incorporation, the reaction became at once easy and K-carboxymethylcellulose was formed. It was necessary therefore to study the effect of varying the ratio of water and ethanol as a reaction medium. The results have been presented in Table 2. The variable has been expressed in terms of water-cellulose ratio, but it indicates the same entities as both the amount of cellulose taken and the total amount of solvent used had been kept the same throughout the series. Two sets of experiments were carried out with 24.5% and 30% KOH concentrations respectively. As was expected somewhat higher degree of substitution was obtained with the higher concentration

TABLE 1.—DIRECT CARBOXYMETHYLATION OF COTTON CELLULOSE EFFECT OF KOH CONCENTRATION.

Concentration of KOH% w/v	Yield of K-CMC* (g)	D.S.	Remarks
17.5	0.3	0.18	Partially soluble in water; insoluble in ethanol
24.5	6.5	0.68	Soluble in water; insoluble in ethanol
30.0	8.0	0.91	
35.0	8.5	1.04	
40.0	8.5	1.06	

*K-carboxymethylcellulose

Purified cotton taken for each experiment 5.0 g; ClCH₂-COOH taken 8 g in 10 ml EtOH; water 5 ml; EtOH 30 ml; steeping temperature 28–30°C; steeping time 2 hr; time for carboxymethylation; 6 hr; temperature for carboxymethylation 30–35°C for first 3 hr and 40–45°C for remaining 3 hr.

TABLE 2.—VARIATION OF DEGREE OF SUBSTITUTION OF K-CARBOXYMETHYL-CELLULOSE WITH WATER/CELLULOSE RATIO.

Concentration of KOH% w/v	Water/cellulose ratio	Yield of K-CMC* (g)	D.S.	Remarks
24.5	0	8.0 (crude)	0.88	Product contained some unreacted fibres
	1.0	6.5	0.68	
	2.0	5.5	0.53	
30.0	3.0	5.1	0.40	Fibre-free product
	0	10.0 (crude)	1.19	
	1.0	8.0	0.91	Product contained some unreacted fibres
	2.0	6.0	0.61	
	3.0	5.5	0.49	

*K-carboxymethylcellulose.

Other conditions were same as described under Table 1.

of potassium hydroxide. But the more remarkable effect was that when the water-cellulose ratio was increased; the degree of substitution became sharply smaller. Another apparent difference in the behaviour (with that in the case of Na-carboxymethylcellulose) will be obvious from the two plots in Fig. 1, where the variation of degree of substitution with water-cellulose ratio has been plotted for (i) 30% KOH concentration and (ii) 17.5% NaOH concentration as had been observed earlier.⁷ It will be seen that in the case of K-carboxymethylcellulose prepared, the degree of substitution is maximum corresponding to zero water-cellulose ratio, that is in absolute alcoholic medium, and then decreases. In the case of Na-carboxymethylcellulose, the D.S. values are relatively lower in absolute alcoholic medium. Maximum degree of substitution was at 1:1 after which it decreased. This apparent anomaly becomes clear when it is noted that KOH concentration in absolute EtOH was higher; whereas in the case of NaOH, solubility is relatively much smaller in absolute EtOH and experiment was carried out with saturated solution only (NaOH for Na-carboxymethylcellulose). It should again be pointed out that maximum degree of substitution obtained in the case of K-carboxymethylcellulose with 30% KOH (1.19) was fairly comparable to that of Na-carboxymethylcellulose obtained under optimum condition (1.23).

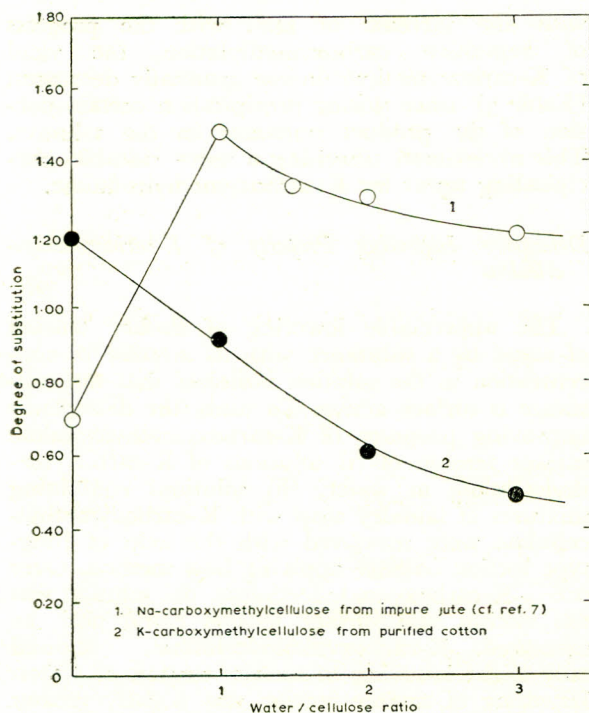


Fig. 1.—Effect of water-cellulose ratio on degree of substitution of product.

Repetitive Carboxymethylation

Complete carboxymethylation of cellulose to K-carboxymethylcellulose, that is, preparation of K-carboxymethylcellulose having a theoretically highest degree of substitution of *three*, has not been possible. In a single treatment only a partially substituted product (D.S. upto 1.19) could be prepared. Like Na-carboxymethylcellulose repetition the process was expected to give much higher substituted K-carboxymethylcellulose. It would be observed that 40% KOH in aqueous-ethanolic medium of carboxymethylation could give a fibre-free product having a high D.S. of 1.06. When carboxymethylation was repeated second time with the product, a K-carboxymethylcellulose having a D.S. of 1.53 was obtained. It has also been seen that 30% KOH in absolute alcoholic medium gave K-carboxymethylcellulose having a D.S. of 1.19. The product contained some unreacted fibres. But when carboxymethylation was performed a second time, K-carboxymethylcellulose having a D.S. of 1.62 was obtained which did not contain any unreacted fibre. Activation seemed to be better in 30% KOH (in absolute alcohol) and therefore in third and fourth stages of carboxymethylation this condition was employed and degrees of substitution obtained were 1.88 and 2.11 respectively. Results of repetitive carboxymethylation are given in Table 3.

In Fig. 2 the variation in D.S. of K-carboxymethylcellulose, prepared in 30% absolute alcohol has been plotted against different stages of carboxymethylation. For comparison another curve presents similar repetitive carboxymethylation for Na-carboxymethylation obtained under the best condition.⁹ The trends of the curves are similar, but the rate of increase of D.S. varies distinctly. In four stages with Na-carboxymethylcellulose a D.S. value of 2.63 and with K-carboxymethylcellulose, a value of 2.11 were obtained. Further, in the case of Na-carboxymethylcellulose it seems that with further stages of carboxymethylation, complete carboxymethylation looks possible; whereas in the case of K-carboxymethylcellulose, it appears impracticable with a reasonable number of repetitions. This is in conformity with the earlier observation on the KOH absorption and subsequent carboxymethylation for K-carboxymethyl cellulose.

It was observed that highly substituted K-carboxymethylcellulose was relatively more soluble in water than Na-carboxymethylcellulose. The concentrated aqueous solution of highly substituted K-carboxymethylcellulose was very sticky towards glass. Solubility of K-carboxymethylcellulose in organic solvents seemed to be increased

TABLE 3.—REPETITIVE CARBOXYMETHYLATION OF COTTON CELLULOSE IN ETHANOLIC MEDIUM FOR HIGHLY SUBSTITUTED K-CARBOXYMETHYL-CELLULOSE.

No. of steps	Amount of fibre or K-CMC* † (g)	Amount of KOH used (g)	Amount of ClCH ₂ COOH (g)	Yield of K-CMC † (g)	D.S.	Remarks
1	5.0	10.5	8.0	10.0 (crude)	1.19	Product contained unreacted fibres. Purified product soluble in H ₂ O and insoluble in EtOH.
2	8.6	9.0	6.9	7.0	1.62	Fibre-free product; highly soluble in H ₂ O and slightly soluble in EtOH.
3	3.5	4.5	3.5	3.0	1.88	Fibre-free product; highly soluble in H ₂ O and slightly soluble in EtOH.
4	1.5	2.3	1.7	1.0	2.11	Fibre-free product; highly soluble in water and slightly soluble in EtOH.

*K-carboxymethylcellulose

†Fibre taken in the first stage only; in other stages K-CMC was taken.

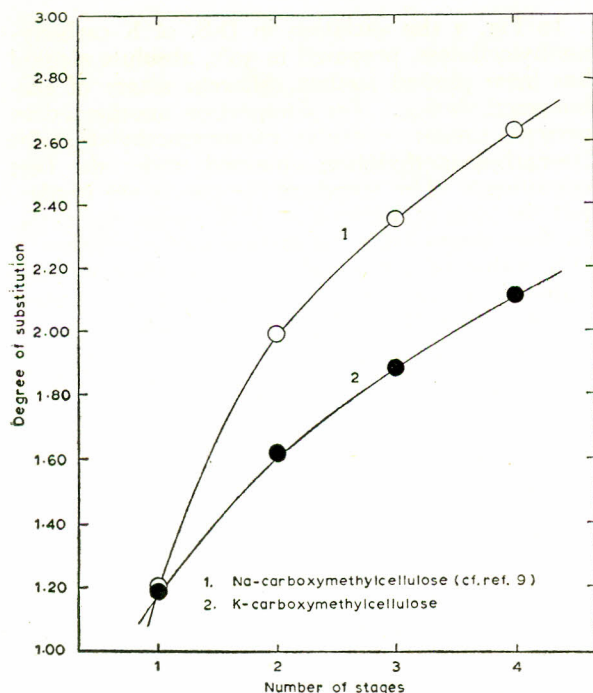


Fig. 2.—Variation of degree of substitution with repetitive carboxymethylation

with the increase of D.S. with the progress of repetitive carboxymethylation, the yield of K-carboxymethylcellulose gradually decreases, (Table 3) since during precipitation certain portion of the product remained in the solution. This necessitates searching a more suitable precipitating agent for K-carboxymethylcellulose.

Detergency Improving Property of K-carboxymethylcellulose

The appreciable lowering of surface tension of water by a substance with its increase of concentration in the solution indicates that the substance is surface active. To study the detergency improving property of K-carboxymethylcellulose surface tension of (i) solutions of K-carboxymethylcellulose in water, (ii) solutions containing mixtures of laundry soap with K-carboxymethylcellulose were measured with the help of Jung-typ torsion balance applying bow method. Over 0.6% K-carboxymethylcellulose, the solution was too viscous and surface tension could not be measured. K-carboxymethylcellulose showed only slight lowering of surface tension of water. Lowering of surface tension was slightly greater for a K-carboxymethylcellulose having high D.S. The top curve in the Fig. 3 indicates the lowering

of surface tension of aqueous solution of a highly substituted K-carboxymethylcellulose against its concentration (given by the top scale of x-axis). Surface tension of aqueous solution of Na-carboxymethylcellulose was measured earlier⁹ in this laboratory which also has been plotted. Lowering of surface tension is rather greater for Na-carboxymethylcellulose solution than K-carboxymethylcellulose solution.

Surface tension of aqueous soap solution is plotted against its concentration (given by the bottom scale of x-axis) in the same figure. When 5% K-carboxymethylcellulose (by wt of soap) is added to the soap, surface tension of the solution is markedly decreased. This decrease in surface tension is marked until critical micelle concentration is reached. Experiments were carried out with K-carboxymethylcellulose having different degrees of substitution. Lowering of surface tension is independent of D.S. of K-carboxymethylcellulose provided D.S. is fairly high and the substance is soluble in water and in the figure only one curve has been shown. Similar experiments were also carried out with soap and Na-carboxymethylcellulose by earlier workers.⁹ The lowering of surface tension was found to be independent of D.S. of Na-carboxymethylcellulose. One curve is given in the figure from which it is clear that the extent of lowering of surface tension of aqueous soap solution with K-carboxymethylcellulose is very much similar to that with Na-carboxymethylcellulose.

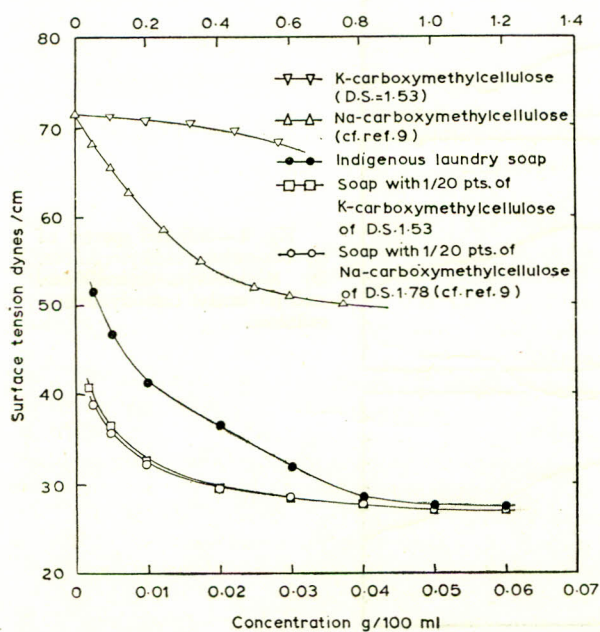


Fig. 3.—Variation of surface tension with concentration.

Emulsifying Properties of Potassium Carboxymethylcellulose

Some cellulose ethers have been successfully used as emulsifying agents for various organic liquid-water systems. Morrison and Campbell¹⁴ reported casually, among other things, that Na-carboxymethylcellulose (prepared from undefined source but apparently from cotton linters, and no mention was made of the D.S.) is a fairly good emulsifying agent for liquid paraffin, but was unsatisfactory in the case of benzene, toluene, vegetable oils (castor, olive, etc.) or cod-liver oil.

Earlier workers¹⁵ in this laboratory studied the emulsifying properties of the systems involving

TABLE 4.—EMULSIFYING PROPERTIES OF PURIFIED K-CARBOXYMETHYLCELLULOSE (D.S.=0.91) FROM COTTON.

pH of soln	Oil (ml)	Water (ml)	Stability
7	5	20	indefinitely
"	10	"	30 days
"	15	"	24 "
"	20	"	10 "
"	"	15	indefinitely
"	"	10	" "
"	"	5	" "
8	5	20	30 days
"	10	"	29 "
"	15	"	23 "
"	20	"	22 "
"	"	15	20 "
"	"	10	19 "
"	"	5	17 "
9	5	20	indefinitely
"	10	"	" "
"	15	"	" "
"	20	"	15 days
"	"	15	5 "
"	"	10	3 "
"	"	5	2 "
10	5	20	30 "
"	10	"	24 "
"	15	"	20 "
"	20	"	indefinitely
"	"	15	5 days
"	"	10	4 "
"	"	5	3 "
11	5	20	indefinitely
"	10	"	" "
"	15	"	" "
"	20	"	" "
"	"	15	" "
"	"	10	" "
"	"	5	5 days
12	5	20	indefinitely
"	10	"	" "
"	15	"	" "
"	20	"	" "
"	"	15	" "
"	"	10	" "
"	"	5	2 days

Oil used, cod-liver oil; concentration of aqueous K-carboxymethylcellulose solution, 2% w/v.

olive and cod-liver oil in water with Na-carboxymethylcellulose. They have shown that Na-carboxymethylcellulose can be successfully utilized as a stabilizer of emulsion between olive oil and water system. The system involving cod-liver oil and water with Na-carboxymethylcellulose was not satisfactory. Maximum stability of cod-liver oil-water system (40 days) obtained at a low oil-water ratio of 1:5.

In the present study emulsifying properties of the systems involving cod-liver oil in water were studied with K-carboxymethylcellulose having a D.S. of 0.91. K-carboxymethylcellulose was highly soluble in water. The results of the stability of different emulsions are presented in Table 4. The percentage concentration of the active agent (K-carboxymethylcellulose) is with reference to the aqueous phase only.

At pH 7, emulsions were stable indefinitely at high oil-water ratios, e.g., 4:3, 2:1, 4:1 and also at a low oil-water ratio of 1:4. Emulsions having oil-water ratio of 1:1, 1:2 and 3:4 were stable for 10, 30, and 24 days respectively. At pH 8, permanent emulsions could not be prepared. Maximum stability of 30 days was obtained at a oil-water ratio of 1:4. Stability decreased with

increasing oil-water ratio. At pH 9, emulsions having oil-water ratio of 1:4, 1:2 and 3:4 were stable indefinitely. With further increase of oil-water ratio, stability decreased gradually. At pH 10, stable emulsions were formed at a oil-water ratio of 1:1. At pH 11 and 12, the only unstable emulsion was at a oil-water ratio of 4:1. Emulsions at these pH were stable at all other oil-water ratios.

It is therefore believed that K-carboxymethylcellulose can be successfully utilized as a stabilizer of emulsions between cod-liver oil and water provided the pH is carefully controlled as shown above.

Water Solubility and Other Physical Properties

Properties of K-carboxymethylcellulose depend primarily on its water solubility, which in turn is believed to vary with the D.S. and change in degree of polymerization of the cellulose chain during the preparation. Provided that the experimental conditions are such as would not allow too much degradation of the chain, K-carboxymethylcellulose having a D.S. of below 0.30-0.40, are very sparingly soluble in water, while a clear solution is obtained with a product having D.S.

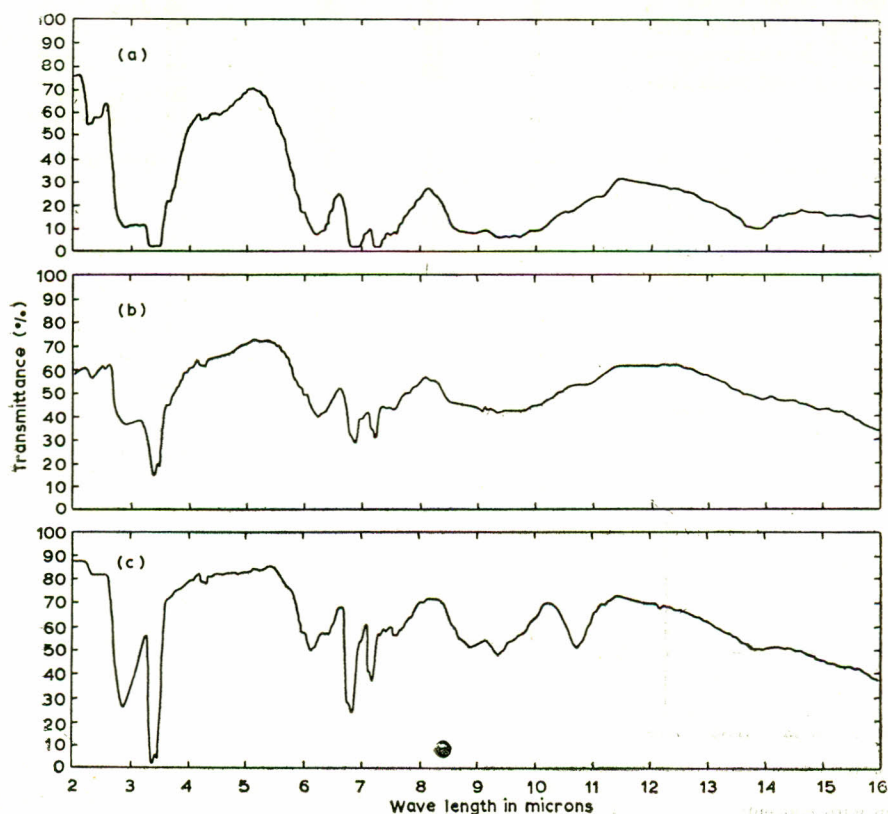


Fig. 4.—Infrared spectra of (a) Na-carboxymethylcellulose, (b) K-carboxymethylcellulose, and (c) uranyl carboxymethylcellulose.

above 0.40. At high concentrations, for example, of 5% solution, a jelly-like mass is obtained. A clear solution is obtained only at a lower concentration. K-carboxymethylcellulose having a high D.S. is highly soluble in water.

Like Na-carboxymethylcellulose, K-carboxymethylcellulose is generally insoluble in organic solvents (e.g. ethanol). K-carboxymethylcellulose of high D.S. is slightly soluble in alcohols. So a certain amount of K-carboxymethylcellulose (having a high D.S.) is always lost during its purification with alcohols.

Aqueous solutions of purified K-carboxymethylcellulose shows pH very close to the neutral point. By acidification with strong acid, free carboxymethylcellulose was precipitated out below a pH of 4. The pH for precipitation of the acid form (carboxymethylcellulose) varies with D.S. and also to some extent with the acid used.

IR Spectra of K (Na and Uranyl) Carboxymethylcellulose

For identification of the product, IR spectrum is very useful. IR spectrum of purified and dried potassium carboxymethyl cellulose (D.S.=1.04) was taken in Nujol in sodium chloride cell with a Beckmann Model IR 4. IR spectrum of K-carboxymethylcellulose is characterized by several well-defined bands. The band of appropriate intensity at 2.90 microns is related to the OH stretching vibration. The broad and intense band at 6.28 microns falls in the general region characteristic of the acid carbonyl group and shows a strong absorption in this region. The heavy, complex absorption at about 8.50-10.50 microns is probably due to vibration involving C—O—C bonds in the skeleton of the molecule.

The spectral absorption of Na-carboxymethylcellulose (D.S.=1.20) and uranyl-carboxymethylcellulose (D.S.=1.04) are also recorded (Fig. 4) for the infra-red. Though the IR spectra of K-

and Na-carboxymethylcellulose are very much similar, bands in the spectrum of uranyl carboxymethylcellulose are much more intense. The broad and intense band at 10.74 microns is due to the characteristic frequency of uranylion.¹⁶

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